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(71) Applicant
Celanese Corporation,
1211 Avenue of the
Americas, New York, New
York, U.S.A.

(72) Inventors
Howard J. Davis,
Willard C. Brinegar,
Phillips L. Scoville,
Peter K. Sullivan

(74) Agent
Carpmaels & Ransford

**(54) Process for Preparing Hollow
Microporous Polypropylene Fibers**

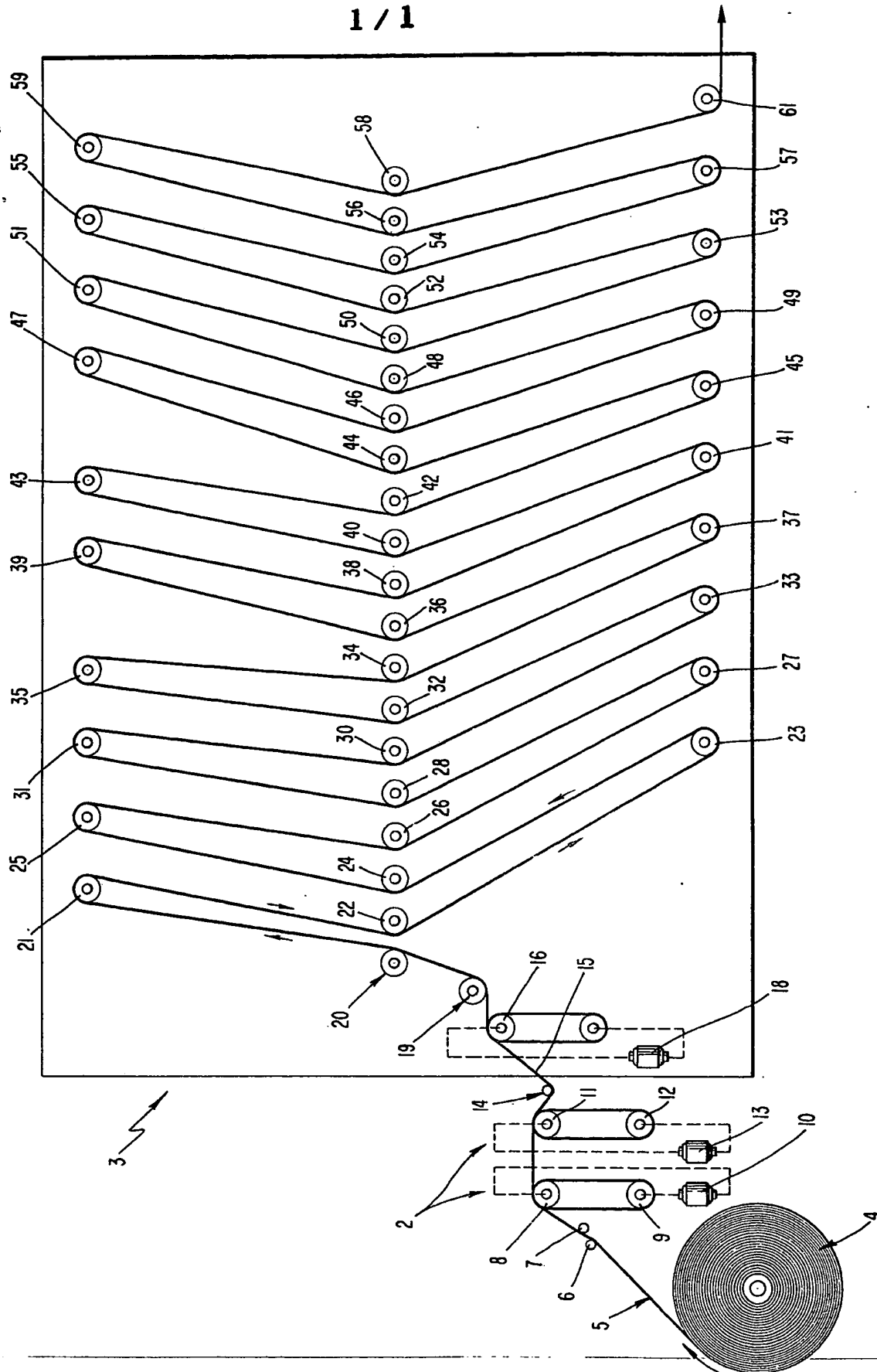
(57) Hollow open-celled microporous polypropylene fibers having an oxygen gas permeability of at least 35 cc/cm².min at 10 psi. are produced by melt spinning isotactic polypropylene at a temperature of at least 230°C to form precursor hollow fibers having an average inner diameter of at least 140

microns, and an average inner diameter to average wall thickness ratio of from 8:1 to 40:1, annealing the precursor fibers at a temperature of 50°C to not greater than 165°C, and subsequently cold stretching, hot stretching and then heat setting the fibers. The resulting hollow microporous fibers exhibit an average inner diameter of at least 100 microns.

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SPECIFICATION

Process for Preparing Hollow Microporous Polypropylene Fibers

Background of the Invention

- The present invention relates to microporous hollow polypropylene fibers and a method for preparing the same. 5
- Hollow porous fibers are well known in the art. The advantages of permeable hollow fibers over permeable films are also well known. For example, porous hollow fibers possess a large surface area per unit volume than a flat film of similar porous configuration. Consequently, there has been a growing tendency to employ, if possible hollow microporous fibers in those applications typically reserved for permeable films. 10
- While the technology for preparing and imparting permeability to hollow fibers and films may at first glance appear to be similar in many respects, there are processing differences peculiar to each technology which lead to significant unpredictable results in permeability performance so as to preclude the wholesale application of film technology to hollow fibers. 15
- For example, U.S. Patent No. 3,801,404 describes a cold stretch/hot stretch process for preparing polypropylene microporous films which includes the steps of extruding a precursor film by a blown film method at a temperature of about 180 to 270°C and taking the film up at take-up speeds of about 30 to 700 ft/min (i.e., 9 to 213 meters/min) and at a drawdown ratio of 20:1 to 200:1. The precursor film is then optionally annealed, cold stretched at a temperature below about 120°C e.g., 20 25°C, hot stretched at a temperature above 120°C and below the polymer fusion temperature e.g., between 130 and 150°C, and finally heat set at a temperature in the range of about 125°C up to less than the polymer fusion temperature e.g., about 130 to 160°C. 25
- If extrusion or melt spinning temperatures of increasingly less than 230°C are employed in preparing the hollow microporous polypropylene fibers of the present invention the structural uniformity of the hollow fibers with respect to inner and outer diameters as well as wall thickness is substantially reduced. Thus, the melt spinning temperature of the hollow fibers represents a process parameter which is not readily translated from film to fiber technology due to the inherent differences between fiber and film configuration, i.e., the concept of uniformity of inner and outer diameter fiber dimensions does not exist in film technology. The melt index of the polypropylene employed to prepare the subject hollow fibers must also be controlled to preserve the structural and dimensional uniformity of the hollow fiber. 30
- Similarly, while the preparation of a film by the blown film method resembles the preparation of a hollow film by the air injection method there is an important difference. The take-up speed in preparing blown precursor films is limited in that at increasingly higher take-up speeds (other processing variables being held constant) the uniformity of the microporous film structure subsequently imparted to the precursor film decreases. Consequently, the process variable of take-up speed cannot be controlled (i.e., increased) in a manner sufficient to impart increasingly higher levels of orientation to the precursor film structure. Higher degrees of orientation up to a certain threshold have a beneficial effect on the ultimate permeability imparted to the film but because of problems of uniformity of pore structure a limit is placed on the degree of orientation which can be imparted via take-up speed control to the precursor film. 35
- When hollow fibers are prepared by the process of the present invention the problems of microporous structural uniformity are substantially reduced and higher take-up speeds can be employed to impart a higher degree of orientation, as determined by the wide angle x-ray diffraction of a (110) plane, to the precursor hollow fibers, thereby imparting a higher permeability potential thereto. 40
- However, this increase in permeability potential is not readily realized in the absence of controlling the inner diameter (I.D.) of the hollow precursor fiber which in turn controls the inner diameter of the subsequently formed hollow microporous fiber. Control of the dimensions of the hollow microporous fiber is a further process variable which cannot be translated from film technology. 45
- U.S. Patent No. 3,558,764 describes a cold stretch process for preparing microporous films which includes the steps of extruding a polymer at specifically defined temperatures to form a precursor film, cooling the precursor film, annealing the precursor film at specifically defined temperatures (i.e., 5 to 100°C below the melting point of the polymer which is about 165°C for polypropylene), cold drawing the resulting film at a specifically defined draw ratio and temperature, and heat setting the cold drawn film at a temperature of about 100 to about 150°C while under tension. 50
- The primary difference in this process from the former cold stretch/hot stretch process is the absence of a hot stretching step. The cold stretch/hot stretch process described above represents an improvement over the cold stretch process of this patent with respect to nitrogen flux. 55
- In contrast, when hollow precursor fibers are annealed, cold stretched, and heat set generally in accordance with the above cold stretch procedures, particularly when the heat set temperature is at or below the initial annealing temperature, the resulting hollow microporous fibers exhibit varying degrees of shrinkage and tend to curl up which is disadvantageous depending on the use for which the hollow fiber is employed. 60
- U.S. Patent No. 4,055,696 describes a similar cold stretch process which is employed to prepare

hollow polypropylene microporous fibers rather than films. This process requires that the size of the pores be kept within a specified range by limiting the degree and temperature of cold stretch to 30 to 200% of the original fiber length and less than 100°C respectively. The resulting cold stretched fibers which have been previously annealed are heat set at a temperature at or above the initial annealing temperature, employed prior to stretching as described above. A separate hot stretching step as employed in the present invention is not included in the preparation of these hollow fibers. Annealed, cold stretched, heat set, hollow fibers prepared in accordance with this patent tend to exhibit varying degrees of shrinkage depending on the relationship of the prior annealing temperature and duration to the heat setting temperature and duration. Moreover, there is no control of the inner diameter of the hollow fibers of this patent to improve oxygen gas permeability thereof.

Japanese Kokai Patent No. Sho 53 [1978]—38715 published April 10, 1978 is directed to an improvement in the method for preparing porous polypropylene hollow fibers disclosed in U.S. Patent No. 4,055,696. The improvement comprises controlling the annealing temperature to be below 155°C and controlling the heat setting temperature after cold stretching to be from 155 to 175°C for from 3 seconds to 30 minutes. This process also fails to employ either a hot stretching step in addition to the cold stretching step as required by the present invention or control of the inner diameter of the hollow microporous fibers to improve oxygen gas permeability.

One particular important use for hollow microporous fibers is as a blood oxygenator as illustrated by U.S. Patent No. 4,020,230 which discloses hollow microporous fibers prepared from polyethylene. As is well known the properties required in a blood oxygenator membrane include good gas permeability with respect to gaseous oxygen and carbon dioxide, chemical stability, blood compatibility or substantially non-thrombogenic behavior in blood containing environments, sufficiently hydrophobic character to serve as a water vapor barrier, ease in manufacture, non-toxicity, relative inertness to body fluids, and mechanical strength and handling properties adequate for facilitating the assembly and use of blood oxygenation devices.

Microporous polypropylene films have previously been employed as blood oxygenation membranes and such films have been found to meet all of the above requirements. However, because of the relatively low surface area of such films, relatively large volumes of blood must be removed from the body to achieve the required oxygen and carbon dioxide gas transfer. In contrast, hollow polypropylene microporous fibers offer the advantage of being able to achieve the same gas transfer using much lower volumes of blood.

There has therefore been a continuing search for hollow polypropylene microporous fibers and a process for preparing the same which exhibit a high oxygen gas permeability. The present invention is a result of this search.

It is therefore an object of the present invention to provide microporous hollow polypropylene fibers which have high oxygen gas permeabilities.

It is a further object of the present invention to provide a process for preparing hollow polypropylene microporous fibers having high oxygen gas permeabilities.

These and other objects and features of the invention will become apparent from the claims and from the following description when read in conjunction with the accompanying drawing.

Summary of the Invention

In one aspect of the present invention there is provided a process for preparing hollow open celled polypropylene microporous fibers having an oxygen flux of at least 35 cc/cm² . min at 10 psi comprising:

(A) melt spinning at a temperature of at least 230°C isotactic polypropylene having a melt index of at least 1 in a manner sufficient to obtain hollow non-porous polypropylene precursor fibers, taking up said precursor fibers at a drawdown ratio of at least about 40, said melt spinning being conducted in a manner sufficient to impart to said precursor fibers after take-up an average inner diameter of at least about 140 microns, an average inner diameter to average wall thickness ratio of from about 8:1 to about 40:1, and a degree of orientation as determined from the half width of the wide angle (110) X-ray diffraction arc, of not greater than 25°C, 65% relative humidity, and zero recovery time, of at least 50%;

(B) annealing the precursor fibers at a temperature between about 50°C and less than 165°C for a period of about .5 second to about 24 hours;

(C) cold stretching the non-porous precursor hollow fibers in the direction of their length at a temperature greater than the glass transition temperature of the precursor fiber and not greater than about 100°C to impart porous surface regions to the walls of the fiber which are perpendicular to the cold stretching direction;

(D) hot stretching the annealed cold stretched hollow fibers of (C) in the same direction of cold stretch at a temperature above the cold stretching temperature and below the melting point of the polypropylene to impart an open celled microporous configuration to the hollow fiber walls, said cold stretching and hot stretching being conducted in a manner sufficient to control the average inner diameter of the resulting hot stretched hollow microporous fibers to be at least 100 microns and to achieve a total degree of combined stretching of from about 80 to about 200%, an extension ratio of

from about 1:3 to about 1:20, and a strain rate of from about 10 to about 200%/minute;

(E) heat setting the resulting hot stretched fibers of (D) under tension to produce dimensionally stable open celled hollow microporous fibers having an average inner diameter of at least 100 microns.

In another aspect of the present invention there is provided hollow polypropylene open celled microporous fibers having an oxygen flux of at least 35 cc/cm² . min at 10 psi prepared by the above process. 5

Brief Description of the Drawing

The figure is a schematic representation of a means for achieving hot stretching in multiple stages.

10 Description of the Preferred Embodiments 10

The hollow microporous fibers of the present invention are prepared from isotactic polypropylene having a weight average molecular weight ranging from about 100,000 to about 750,000, and a melt index of not less than about 1 (e.g., not less than about 5), typically from about 1 to about 30 or higher, preferably from about 3 to about 15 and most preferably from about 5 to about 10.

15 The term melt index as used herein is defined as the value obtained by performing ASTM D-1238 15 under conditions of temperature, applied load, timing interval and other operative variables which are specified therein for the particular polymer being tested, i.e., polypropylene.

If a fiber is prepared from polypropylene having a melt index increasingly below about 1, e.g., 0.5, the fiber exhibits an increasing tendency to break or split and an increasingly greater fluctuation in the 20 uniformity of the inner diameter and cross-section of the fiber. 20

The density of the polypropylene should be about 0.90 gm/cc.

The isotactic polypropylene is converted to a hollow precursor fiber by melt spinning. The molten polymer is caused to flow through one or more orifices (i.e., jets) of a spinneret which is capable of imparting the desired continuous hollow configuration to the fiber. For instance, in the preferred 25 embodiment the melt is caused to flow through one or more annular dies having a needle extending 25 into each central portion thereof. A gaseous stream is then passed through the needle as the melt is pumped through the annular die thereby imparting a hollow configuration to the fiber. Alternatively, the hollow lumen of the fiber may be formed by passing the molten polymeric material through an annular orifice or a solid core capable of causing the desired hollow structure to be formed.

30 The temperature at which the polypropylene is extruded, i.e., melt spun (assuming other spin 30 variables as described herein are employed) should be at least 230°C preferably from about 240 to about 280°C, and most preferably from about 240 to about 250°C.

If an extrusion temperature increasingly below about 230°C is employed the uniformity of the fiber with respect to inner and outer diameters increasingly deteriorates. In contrast precursor films 35 employed in the cold stretch/hot stretch process of U.S. Patent No. 3,801,404 can be prepared at 35 extrusion temperatures as low as 180°C. At extrusion temperatures increasingly higher than about 280°C the spin stress applied to the extruding polymer must be substantially increased, and there is a danger of polymer degradation.

When an air injection hollow fiber spinneret is employed the jet diameter, air flow rate, take-up 40 speed, extrusion velocity, and drawdown ratio are controlled in a manner sufficient to achieve a 40 precursor hollow polypropylene fiber having an average inner diameter and average wall thickness with dimensions as described herein and a degree of orientation of not greater than about 25° as determined by the half width of a (110) wide angle X-ray diffraction arc.

The degree of fiber molecular orientation is determined by superimposing the fibers in alignment 45 to a thickness of 50 mg/cm². X-rays are then irradiated to the fibers in a direction perpendicular to the 45 axial direction of the fibers and the half-width of a (110) wide angle diffraction arc is recorded on film.

The angular spread of this (110) diffraction arc is then determined and should not be greater than 25°.

The dimensions (i.e., inner and outer diameters) and wall thickness of the hollow fibers produced can be controlled in several ways. Initially, the diameter of the die and inert gas pressure selected will 50 govern the inner and outer dimensions respectively of fibers produced, as modified by the degree of 50 enlargement of fiber dimensions by release from the metered pressure of extrusion through the spinneret. Diameter and wall thickness can also be varied by varying the pressure of extrusion through the spinneret and the take-up speed at which the fibers are drawn away from the spinneret. Changes in one of these values can be compensated for by changes in the other to achieve the desired results.

55 While the above processing parameters are controlled with a view toward achieving an inner 55 diameter within a limited range they are also controlled to impart the proper morphology to the precursor fiber to insure that subsequent processing achieves a microporous structure having a suitable gas permeability.

Accordingly, the melt spinning or melt extrusion step of the process is conducted at a relatively 60 high "drawdown" or "spin draw" ratio so that the hollow fibers are spin-oriented as they are formed. 60 Drawdown ratio is defined as the ratio of the velocity of the initial take-up speed of the hollow fibers to the linear velocity of extrusion of the polymer through the spinneret orifice. The drawdown ratio used in the process of the present invention is at least 30, preferably at least 40, (e.g., from about 40 to about

100) and may be as high as about 700. Take-up speeds employed to accomplish the requisite drawdown ratios are generally at least about 200 meters/minute, typically from about 200 to about 1000 meters/minute and preferably about 200 to 500 meters/minute. Typically high shear forces are developed in the polymeric material which are not relaxed prior to fiber solidification.

5 The air flow rate i.e., the rate at which the air is passed through the needle in the central portion of the jet hole will vary depending on the number of jet holes in the spinneret and is typically controlled to be from about 5 to about 70 cc/min/jethole, and preferably from about 10 to about 50 cc/min/jethole. 5

The temperature of the air as it exits the air injection spinneret is typically the same temperature as the melt spinning temperature of the polymer. 10 10

The hollow spin oriented precursor fibers may optionally be quenched by passing them through a current of gas, such as ordinary air at room temperature or through an inert liquid such as water so that rapid cooling of the just-spun hollow fiber results. The temperature of the quenching medium can be as high as 80°C and as low as 0°C (e.g., 0 to 40°C) depending on other spinning parameters. However, 15 the preferred quench temperature is 25°C and passage of the just-spun fibers through ambient air results in an adequate quench when the take-up roll is located about 5 to about 10 feet or more from the spinneret. 15

The resulting precursor hollow polypropylene fiber is nonporous and exhibits a crystallinity of at least 30%, preferably at least 40%, and most preferably at least 50% (e.g., about 50 to about 60% or more). Percent crystallinity is determined from the relationship: 20 20

$$\% \text{ Crystallinity} = \frac{\bar{V}_a - \bar{V}}{\bar{V}_a - \bar{V}_c} \times 100$$

wherein \bar{V}_a is the specific volume of the 100% amorphous polymer, \bar{V}_c is specific volume of the 100% crystalline polymer and \bar{V} is the specific volume of the sample of interest. The specific volume of a polymer is $1/D$ where D is the density of the polymer. The density of the polymer is measured by means of a density gradient column as described in ASTM D-1505-68. The precursor hollow polypropylene 25 fibers should also exhibit an elastic recovery at zero recovery time when subjected to a standard strain (extension) of 50% at 25°C, and 65% relative humidity, of at least about 50%, preferably at least about 60%, and most preferably at least about 65%. 25

Elastic recovery as used herein is a measure of the ability of structured or shaped articles, such as hollow fibers, to return to their original size after being stretched. 30 30

The elastic recovery value is determined with an Instron Tensile Tester operating at a strain rate of 100%/minute. After the fiber is extended to the desired strain value, the jaws of the apparatus are reversed at the same speed until the distance between them is the same as at the start of the test, i.e. the original gauge length. The jaws are again immediately reversed, and are stopped as soon as the stress begins to increase from the zero point. The elastic recovery is then calculated as follows: 35 35

$$\text{Elastic Recovery \%} = \frac{\left(\begin{array}{c} \text{Total length} \\ \text{when extended} \end{array} - \begin{array}{c} \text{Final distance} \\ \text{between jaws} \end{array} \right)}{\text{Length added when extended}} \times 100$$

Measurements with the Instron Tensile Tester are conducted at room temperature, e.g. 25°C, in air at 65 percent relative humidity.

Although a standard strain of 50% is used to identify the elastic properties of the precursor fibers, such strain is merely exemplary. In general, such precursor fibers will have elastic recoveries higher at strains less than 50% and somewhat lower at strains substantially higher than 50%, as compared to their elastic recovery at a 50% strain. 40 40

The above processing conditions are controlled to provide precursor hollow polypropylene fibers having an average inner diameter (I.D.) of at least 140 microns, preferably from about 140 to about 400 microns or higher most preferably from about 200 to about 300 microns. The above average inner diameters have been found to be necessary for imparting a high gas permeability potential to the precursor hollow fibers. Where high gas permeability is not a controlling factor in the desired end use of hollow fibers the inner diameters may be reduced to below 140 microns. 45 45

The dimensions of the hollow fibers are expressed as an average value since such dimensions will vary to some extent depending on where, along the fiber length, the dimensions are determined. Consequently the average inner and outer diameters are determined by cutting cross-sections of the fiber at 6 inch intervals for a total of 5 intervals along the fiber length and determining the fiber dimensions at each of these intervals. The fiber sections are then immersed in standard optical immersion oil and the dimension at each interval is determined using an optical microscope and optical scaling. The results are then averaged to determine the average inner and outer diameters. 50 55

The minimum wall thickness of the precursor hollow fibers should be sufficient so as to not be

readily ruptured or otherwise undergo physical deterioration at a rate that would make their use unattractive after they have been rendered microporous by the procedures described herein. The maximum wall thickness of the hollow fibers is limited by the degree of permeability sought to be imparted to the final product.

- 5 The measurement of average wall thickness is accomplished by determining the average outer diameter and average inner diameter of the fiber and taking as the wall thickness one half of the difference in these average diameters. 5

Furthermore, the average wall thickness may be expressed as a function of the average inner diameter of the hollow fiber. The ratio of the average inner diameter of the hollow precursor fiber to its average wall thickness can vary from about 8:1 to about 40:1, preferably from about 10:1 to about 30:1 and most preferably from about 10:1 to about 20:1. More specifically an average precursor fiber wall thickness of at least 10 microns and typically from about 10 to about 25 microns is preferred. 10

While it is the inner diameter, and associated wall thickness, of the final microporous hollow fiber product which are believed to be a primary controlling factor of gas permeability it is the inner diameter and wall thickness of the precursor hollow fiber which predetermines the maximum obtainable inner diameter and wall thickness of the final product. This results from the fact that the inner diameter of the precursor fiber shrinks about 25% when subjected to the two-stage stretching process described herein. The average wall thickness of the hollow microporous fibers remains substantially unchanged by processing in comparison to the precursor fiber although it may be reduced to a small extent. 15 20

The hollow precursor fibers are next subjected to a heat treatment or annealing step in which the amount of crystallinity and/or their crystal structure is improved. More specifically, this step of the process increases crystallite size and removes imperfections in the molecular alignment. The annealing is conducted for a balance of time and temperature so as to achieve the desired improvements as described above and yet sufficient to avoid destroying or adversely affecting the precursor polymer structure (e.g. orientation and/or crystallinity). 25

The preferred annealing temperatures can vary from about 130 to about 145°C, for a period of about 30 minutes. As the annealing temperature is increased above about 145°C at time during which the precursor fiber is annealed is accordingly reduced. Conversely, as the annealing temperature decreases below 130°C, increasingly longer annealing times are employed. 30

If the annealing temperature increasingly exceeds 145°C at an annealing time of 30 minutes, the precursor polymer fiber structure will be adversely affected and the gas permeability potential of the precursor fiber will be increasingly reduced. If the annealing temperature is increasingly less than 130°C for 30 minutes, the gas permeability potential of the precursor fiber will also be increasingly reduced. 35

In view of the above, the annealing is conducted for periods of about 0.5 second to about 24 hours at a temperature of from about 50°C to less than the melting point of the polypropylene (i.e. 165°C based on differential scanning calorimetry).

The annealing step may be conducted in a tensioned or tensionless state by depositing the precursor fiber in a static condition in a heating zone which is maintained at the requisite elevated temperature, or by continuously passing the precursor fiber through the heating zone. For example, the elevated temperature may be accomplished by the use of a conventional circulating air oven, infra-red heating, dielectric heating, or by direct contact of the running fiber with a heated surface which is preferably curved to promote good contact. The precursor fiber may be continuously passed through a jacketed tube or shroud which radiates heat at the desired temperature. Alternatively, the precursor fiber may be wound under substantially no stress on a bobbin while undergoing annealing, or simply placed in the heating zone in a loose state, such as a skein of continuous fibers. For best results it is recommended that the hollow fiber be maintained at constant length during the annealing step, i.e., under tension sufficient to prevent a longitudinal extension or shrinkage of greater than about 5%. This can be achieved by passing the fibers in the direction of their length over and about a first stress isolation device through a heating zone maintained at the appropriate temperature and then over and about a second stress isolation device. Each stress isolation device may conveniently take the form of a pair of skewed rolls. Control of the ratio of the surface speeds of the two sets of rolls permits isolation and control of the stress of the fibers between the rolls as they undergo annealing. 40 45 50

55 The resulting non-porous precursor hollow fiber is then subjected to a two-stage stretching process and subsequently heat set. 55

In the first stretching stage referred to herein as "cold stretching", the precursor hollow fibers are stretched at a temperature above the glass transition temperature (T_g) of the precursor fiber and not greater than about 100°C. Typical cold stretching temperatures can vary from about 0 to about 100°C, preferably from about 15 to about 70°C, and conveniently at room temperature, e.g., 25°C. 60

The temperature of the fiber itself is referred to as the stretch temperature.

It is recognized by those skilled in polymer technology that the glass transition temperature (T_g) is the temperature at which the structure of a wholly or partially amorphous polymeric material changes from a vitreous state to a viscoelastic state. The glass transition temperature of polypropylene is measured by plotting its specific heat against temperature and noting the temperature at which 65

there is a change in the slope of the curve. This measurement is commonly termed thermomechanical analysis and can be carried out with commercially available instruments such as a Thermomechanical Analyzer Model No. 990 manufactured by Du Pont. The glass transition temperature is also referred to as the second-order transition temperature.

- 5 Cold stretching imparts porous surface regions or areas to the fiber wall which are elongated perpendicular to the stretch direction. 5

The second stretching stage, referred to herein as hot stretching, is conducted at a temperature above the cold stretching temperature but less than melting point of the precursor fiber before or after cold stretching i.e. the first-order transition temperature, as determined by differential scanning calorimeter analysis.

- 10 10

Typical hot stretching temperatures will be greater than about 100°C and can vary from about 105 to about 145°C, preferably from about 130 to about 145°C, and most preferably from about 135 to about 145°C. Again the temperature of the fiber itself being stretched is referred to herein as the hot stretch temperature.

- 15 When the hot stretching temperature employed is increasingly less than 130°C increasingly higher degrees of shrinkage in the final fiber product are observed. 15

Hot stretching opens the porous surface regions imparted by the cold stretching to form an open celled microporous structure.

- 20 The stretching in the two stretching stages must be consecutive, in the same direction and in that order, i.e., cold stretched and then hot stretched but may be done in continuous, semi-continuous, or batch process as long as the cold stretched fiber is not allowed to shrink to any significant degree (e.g., not greater than about 10% based on the initial precursor fiber length). 20

- 25 The sum total degree of stretching in the above cold and hot stretching stages can vary from about 80 to about 200% (e.g., about 80 to about 155%), and preferably from about 85 to about 120% (e.g., about 90%), based on the initial length of the precursor fibers. When the total degree of stretch is increasingly less than about 80%, the resulting oxygen gas permeability at 10 psi is increasingly less than about 35 cc/cm² . min. The ratio of the degree of stretch of the first (cold) to second (hot) stretching stages, is referred to herein as the extension ratio. The extension ratio can vary from about 1:3 to about 1:20 preferably about 1:3 to about 1:10 (e.g., 1:3 to about 1:5). 25

- 30 It is to be understood that the particular total degree of stretch and extension ratio are selected from the above ranges in a manner sufficient to control the final average inner diameter of the hot stretched microporous fibers within the limits described herein. 30

- 35 The strain rate, i.e., the degree of stretch per unit time at which the precursor fibers are stretched during both stretching stages is preferably the same for each stage and can vary from about 10 to about 200%/minute, preferably from about 10 to about 100%/minute and most preferably from about 15 to about 30%/minute (e.g., about 20%/minute). 35

At the preferred total degree of stretch of about 80 to about 120% the preferred extension ratio is 1:3 to about 1:5, e.g., 20% cold stretched and from about 60 to about 100% hot stretched.

- 40 The cold and hot stretching of the precursor fibers may be performed in any convenient manner using known techniques. For example, the hollow fibers can be stretched on a conventional draw frame located in a heating zone which controls the temperature of the fibers during stretching. Alternatively the fibers may be cold and hot stretched in a continuous fashion by means of two sets of stress isolation devices (one set for each stage) similar to those described in connection with the annealing step. 40

- 45 Accordingly, precursor fibers may be wound several times about a first pair of skewed rolls, passed through a heating zone, wherein for example they are contacted with a suitable heating device or medium and maintained at a suitable cold stretch temperature and wound several times about a second pair of skewed rolls. This arrangement permits isolation and control of the longitudinal stress of the fibers between the two pairs of rolls during cold stretching. The fibers are then passed through a similar set of paired skewed rolls while heated to the appropriate hot stretch temperature. The differential ratio of the surface speed of each of the second pair of rolls to the surface speed of each of the first pair of rolls determines the stretch ratio and strain rate which are adjusted accordingly. 50

- 55 It is to be understood that in a continuous process the cold stretch fibers may undergo shrinkage as they pass from the cold stretching stage to the hot stretching stage. This can occur as a result of warm-up of the cold stretched fibers as they enter the hot stretching zone, such as a forced hot air oven, but before they are actually hot stretched. Consequently, it is preferred to insert a tensioning device between the cold and hot stretching stages to prevent shrinkage of greater than about 5% based on the cold stretch fiber length. Such tensioning device may conveniently take the form of a single pair of skewed rolls. 55

- 60 The heating zones which heat the precursor fibers to the appropriate cold stretch or hot stretch temperature are the same as described for annealing prior to cold stretching and may conveniently take the form of a gas such as air, heated plate, heated liquid and the like. The preferred heating device is a forced hot air oven which houses the stretching means. 60

- 65 After the above described cold and hot stretching operations, the stretched fibers are heat set or annealed while in the stretched condition at a temperature from about 125°C up to less than the 65

fusion temperature of the polymer. As is known to those skilled in the art, the fusion temperature may be determined by a standard differential scanning calorimeter or by other known apparatus which can detect thermal transitions of a polymer. The preferred heat setting temperatures can vary from about 130 to about 145°C. The most preferred heat setting temperature is the same as the temperature employed during hot stretching. Heat setting does not change the fiber dimensions as they exist subsequent to hot stretching.

The heat setting step may be conducted in a batch process as in an oven or autoclave, or in a continuous manner. For instance, the hollow microporous fibers may be rewound on a bobbin after hot stretching, and subjected to the annealing operation in that form. Alternatively, the hollow fibers may be stretched and heat set in a continuous procedure by means of two pairs of driven rolls downstream to the stretching rolls traveling at the same speeds with the material between the rolls continuously passing at constant length after hot stretching through the heating zone. Consequently, the stretching and heat setting steps of the process may be carried out sequentially or they may be combined in a single in line operation.

The heat setting treatment should be carried out while the fibers are being held under tension, i.e., such that the fibers are not free to shrink or can shrink only to a controlled extent not greater than about 15% of their stretched length, but not so great a tension as to stretch the fibers more than an additional 15%. Preferably, the tension is such that substantially no shrinkage or stretching occurs, e.g., less than 5% change in stretched length.

The period of heat setting treatment which is preferably carried out sequentially with and after the hot stretching operation, should not be longer than 0.1 second at the higher heat setting temperatures and, in general, may be within the range of about 5 seconds to 1 hour and preferably about 1 to 30 minutes.

Since the most preferred heat set temperature is the same as the hot stretching temperature, it is preferred to conduct both hot stretching and heat setting in the same heating means, such as a hot air oven, in which case the total residence time in the oven for hot stretching and heat setting steps can vary from about 10 to about 45 minutes, and preferably from about 25 to about 35 minutes (e.g., 35 minutes) for hot stretching temperatures of about 130 to about 145°C.

The function of the heat setting step is to improve the thermal stability of the microporous structure and reduce shrinkage of the fibers.

In an alternative embodiment the hot stretching and heat setting steps may be combined into a single step.

In this embodiment hot stretching is achieved using a plurality of discrete sequential hot stretching operations at the appropriate hot stretch temperature. For example, after the fibres have been cold stretched they are guided into a means capable of stretching the fibers in an incremental fashion while maintained at the appropriate hot stretch temperature so that the total degree of stretch of each increment adds up to the desired degree of total hot stretch.

The multiple stage hot stretching means may conveniently take the form of a plurality of rolls disposed in an oven. Preferably the rolls are disposed in a festoon configuration similar to that described in U.S. Patent No. 3,843,761, the disclosure of which is herein incorporated by reference. The employment of a festoon arrangement is preferred in that it provides extended exposure time in the oven containing the multiple stage hot stretching means and thereby eliminates the need for any heat setting step after hot stretching is concluded.

To illustrate a preferred method for achieving multiple stage hot stretching and combined heat setting, reference is made to the figure. Nonporous precursor fibers 5 which have been annealed are unrolled from a supply roll 4, over idler rolls 6 and 7 into a cold stretching zone generally denoted at 2. The cold stretching apparatus includes two pairs of shewed rolls 8-9 and 11-12 which are driven at peripheral speeds S_1 , S_2 , S_3 and S_4 , respectively, by suitable driving means 10 and 13 to achieve the desired degree of cold stretch as described herein. For purposes of illustration the cold stretch temperature is at room temperature and no heating or cooling means is required for this stage. If desired, however, suitable temperature control means may be supplied as described herein. The cold stretched fibers, now denoted 15, are guided into hot stretching means generally indicated at 3 over one or more idler rolls 14. Nip rolls are not employed since they tend to crush the hollow fibers which is disadvantageous to the final product. The hot stretching means 3 comprise a single set of skewed rolls 16 and 17 and a plurality of additional multiple hot stretching rolls disposed in an oven in a festoon configuration. In order to minimize the unsupported fiber length between adjoining hot stretch rolls, which is relatively long in the preferred festoon arrangement, at least one idler roll is provided between adjoining hot stretch rolls.

The single set of skewed rolls 16 and 17 helps to maintain tensioning of the cold stretched fibers by controlling the peripheral speeds S_5 and S_6 respectively thereof. Tensioning prevents shrinkage, sag and the like caused by any preheating of the fibers as they pass into the oven but before they are hot stretched. Such tensioning helps to avoid any decrease in cold stretched fiber properties caused by preheating. Although this tensioning step, to prevent fiber relaxation, may result in a small amount of stretching, the primary effect of this procedure is tensioning and the peripheral speeds S_5 and S_6 are controlled accordingly by drive means 18 to maintain constant length between cold stretching and hot

stretching zones. Thus this procedure is but a preferred embodiment of a means for maintaining fiber tension prior to hot stretching. Other methods that prevent fiber relaxation during warm-up of the fibers prior to hot stretching may be employed.

5 The tensioned cold stretched fibers 15 are then conveyed downstream over idler rolls 19 and 20 onto a first hot stretch roll 21. The fibers are hot stretched for the first time between roll 21 and the second tensioning roll 16. This occurs because the downstream first hot stretch roll 21 is rotated at a peripheral speed S_7 which exceeds the peripheral speed S_6 imparted to the fibers by roll 16. It should be noted that an idler roll 19 is disposed between rolls 16 and 21 in order to decrease the unsupported fiber length during the hot stretching step.

10 This procedure is continued for as many discrete steps as may be preferred. For example, the fibers are stretched for a second time between the first hot stretch roll 21 and a second hot stretch roll 23. In this second hot stretch step, the peripheral speed of the second hot stretch roll 23 is S_8 . Peripheral speed S_8 is greater than the peripheral speed of S_7 of the first hot stretch roll 21. Thus, the fibers are hot stretched in the second hot stretch step at a hot stretch ratio of S_8/S_7 . Again, in order to minimize the unsupported fiber length at least one idler roll 24 is disposed between the second and third hot stretch rolls 23 and 25. In a preferred embodiment, illustrated in the figure, the idler rolls are disposed approximately midway between adjoining hot stretch rolls.

15 In the embodiment illustrated in the figure twenty stretching steps, which occur sequentially, are provided. As illustrated in the figure, in order to provide 20 stretching steps, 21 hot stretch rolls are required. It should be noted that the second tensioning roll 16 is equivalent to the first hot stretching roll. In general, in the hot stretching apparatus of the preferred embodiment, $(n+1)$ hot stretch rolls are required to provide n sequential hot stretch steps. Preferably 2 to 40 stretching steps are preferred in the multiple stage hot stretching operation.

20 Two preferred methods may be employed to provide continuously-increasing peripheral speed with each additional downstream hot stretch roll. In one preferred embodiment, all the rolls are driven by one common drive mechanism. Thus, each hot stretch roll is driven at the same rotational speed. However, each hot stretch roll is of different diameter. More specifically, each additional downstream hot stretch roll has a greater diameter than the upstream roll adjacent to it. Thus, roll 23 is of greater diameter than roll 21 and roll 57, the downstream most hot stretch roll has a diameter greater than the diameter of the next to last downstream roll 55. As those skilled in the art are aware, the peripheral or surface speed of a larger diameter roll rotating at its center at the same speed as a roll of smaller diameter is greater than the smaller roll. Therefore, the employment of increasingly greater diameter rolls serves the purpose of providing differential peripheral speeds between adjoining hot stretch rolls.

25 A second preferred method for providing a differential increasing peripheral speeds between adjoining hot stretch rolls is to provide separate driving means for each roll. In this preferred embodiment, each roll may be of the same diameter. The increasing speed of adjoining downstream hot stretch rolls then becomes a function of the power imparted to each roll.

30 It will be understood that the process variables described above in connection with the single increment hot stretching procedure are applicable to the multistage hot stretching operation with the exception that obvious modifications may be necessary in going from the former to the latter. For example, as described above, the total degree of hot stretch in both stretching embodiments is the same with the exception that in multiple stage hot stretching the total degree of stretch is achieved in several, preferably equal, increments. Also the strain rate for each hot stretching increment is preferably controlled to provide a total residence time in the multiple hot stretching zone approximately equal to the combined resistance time for the heat setting employed in connection with single increment hot stretching and that obtained when the strain rate is within the ranges described herein for hot stretching in a single stage.

35 The resulting hollow microporous fibers possess an average inner diameter as defined herein of about 100 to about 300 microns or higher, and preferably from about 200 to about 300 microns (e.g., 250 microns).

40 The average wall thickness of the hollow microporous fibers does not change substantially from that of the corresponding precursor fiber and the change in the average inner diameter to average wall thickness ratio of the microporous fibers from the precursor fibers is due to the reduction in the precursor fiber average diameter caused by stretching.

45 The average inner diameter to average wall thickness ratio of the hollow microporous fibers will vary from about 7:1 to about 35:1, and preferably from about 10:1 to about 30:1. The particular wall thickness achieved is predetermined by the precursor fiber wall thickness which as described above will depend on the end use for which the fibers will be employed and the pressure to which they will be subjected. Preferably, the particular wall thickness selected is the minimum which will withstand normal operating conditions for a particular end use without undergoing physical deterioration at an unacceptable rate.

50 When the hollow microporous fibers are employed for blood oxygenation the wall thickness can vary from about 10 to about 30 microns and the average inner diameter can vary from about 200 to about 400 microns and still exhibit high gas permeabilities and structural integrity.

65 When the average inner diameter of the hollow microporous fiber is decreased below 100

microns for a given wall thickness the gas permeability at 10 psi decreases substantially.

When the average inner diameter of the microporous hollow fibers of the present invention is at least 100 microns, and the inner diameter to wall thickness ratio is not less than about 7:1, such hollow fibers will exhibit an oxygen flux at 10 psi of at least 35 cc/cm² . min, typically from about 35 to about 85 cc/cm² . min, and preferably from about 40 to about 60 cc/cm² . min.

The oxygen flux J_g is determined by passing oxygen gas through a hollow fiber module which is discussed in greater detail in the examples. The hollow fiber module permits gas to be passed under pressure (e.g., 10 psi) through the interior of the hollow fibers, through the microporous hollow fiber wall and collected. The volume of the gas collected over a period of time is then used to calculate the gas flux in cc/cm² . min of the hollow fibers according to the equation:

$$J_g = \frac{V}{(A)(T)}$$

wherein V is the volume of gas collected; A is the internal surface area of the hollow fibers determined from the equation $A = n\pi dl$ wherein n is the number of hollow fibers, d is the inner diameter of the hollow fibers in centimeters, and l is the fiber length in centimeters; and T is the time in minutes it takes to collect the gas.

The pores of the hollow microporous fibers are essentially interconnected through tortuous paths which may extend from one exterior surface or surface regions to another, i.e., open-celled. This term "open-celled structure" signifies that the major portion of the void or pore space within the geometric confines of the walls of the hollow fiber is accessible to the surfaces of the fiber walls.

Further, the porous hollow fibers of the present invention are microscopic, i.e., the details of their pore configuration or arrangement are described only by microscopic examination. In fact, the open cells or pores in the fibers are smaller than those which can be measured using an ordinary light microscope, because the wavelength of visible light, which is about 5000 Angstroms (an Angstrom is one ten-billionth of a meter), is longer than the longest planar or surface dimension of the open cell or pore. The microporous hollow fibers of the present invention may be identified, however, by using electron microscopy techniques which are capable of resolving details of pore structure below 5000 Angstroms.

The open-celled microporous hollow fibers prepared in accordance with the present invention have an average pore size of 100 to 5000 Angstroms, and more usually 150 to 3000 Angstroms.

These values are determined by mercury porosimetry, as described in an article by R. G. Quynn, on pages 21—34 of Textile Research Journal, January, 1963. Alternatively, an electron micrograph of the fibers can be taken and pore length and width measurements are obtained by using an image analyzer or ruler to directly measure the length and width of the pores thereof, usually at 5000 to 12,000 magnification and scaling down to appropriate size. Generally, the pore length values obtainable by electron microscopy are approximately equal to the pore size values obtained by mercury porosimetry.

The hollow microporous fibers of the present invention are also characterized by a reduced bulk density, sometimes hereinafter referred to simply as a "low" density. The bulk density is also a measure of the increase in porosity of the fibers. That is, these microporous hollow fibers have a bulk or overall density lower than the bulk density of corresponding precursor hollow fibers composed of identical polymeric material, but having no open-celled or other voidy structure. The term "bulk density" as used herein means the weight per unit of gross or geometric volume of the fiber, where gross volume is determined by immersing a known weight of the fiber in a vessel partly filled with mercury at 25°C and atmospheric pressure. The volumetric rise in the level of mercury is a direct measure of the gross volume. This method is known as the mercury volumenometer method, and is described in Encyclopedia of Chemical Technology, Vol. 4, page 892 (Interscience, 1949).

Thus the hollow microporous fibers have a bulk density no greater than 95% and preferably about 40 to about 85% of the precursor fibers. Stated another way, the bulk density has been reduced by at least 5% and preferably about 15 to about 60%. The bulk density is also a measure of porosity in that, where the bulk density is about 40 to 85% of the precursor fiber, the porosity has been increased by 60 to 15% because of the pores or holes.

The final crystallinity of the microporous hollow fibers is preferably at least 35%, more preferably at least 45% and more suitably about 50 to 100% as determined by the aforementioned density method.

The hollow microporous fibers also have a breaking elongation (ASTM D-123-70) of not less than about 50%, and preferably not less than about 100%.

The surface area of the hollow microporous fibers described herein will exhibit a surface area of at least 15 m²/gm and preferably from about 20 to about 60 m²/gm.

Surface area may be determined from nitrogen or krypton gas adsorption isotherms using a method and apparatus described in U.S. Patent No. 3,262,319. The surface area obtained by this method is usually expressed as square meters per gram.

In order to facilitate comparison of various materials, this value can be multiplied by the bulk

density of the material in grams per cc resulting in a surface area quantity expressed as square meters per cc.

The microporous hollow polypropylene fibers of the present invention in addition to having good gas permeability also exhibit good liquid flux and are suitable for a number of applications including blood oxygenation, ultra filtration, dialysis, separation of gamma globulin from blood, for ascites treatment, as well as a variety of other applications which employ hollow microporous fibers. For certain uses it may be desired to render the normally hydrophobic hollow microporous fibers of the present invention hydrophilic. This can be achieved by any means known to those skilled in the art such as by the impregnation of the pores of the fibers with a suitable surfactant such as high molecular-weight, non-ionic surfactants available under the trade name PluronicTM from Wyandotte Chemicals Corp. which are prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Other surfactants include the series of non-ionic surface-active agents available under the trade name TweenTM which are polyoxyalkylene derivatives of hexitol anhydride partial long chain fatty acid esters. Alternately, the fibers may be treated with sulfuric acid, chlorosulfonic acid or other such agents to render the fibers hydrophilic.

To employ the hollow fibers for blood oxygenation, bundles of hollow fibers containing the desired number of fibers can be prepared by applying an adhesive to each end of a group of prearranged parallel hollow fibers. The bundled fibers are then preferably inserted into an elongated fluid-tight tubular casing assembly formed of a suitable material such as steel. Each end of the bundled fibers communicates to the outside of the casing while at either end of the casing a means for sealing each end of the fiber bundle to the ends of the casing is provided. Thus, blood can be pumped through the hollow fibers. The tubular casing is further provided with valves which open into the interior of the casing and to the outer surface of each of the fibers in the bundles, so as to provide a means for circulating oxygen gas about the hollow fibers. Although the fiber bundle should be packed as tightly as possible, it should be packed loosely enough to allow a gas to pass between the individual fibers and effectively surround each hollow fiber.

The oxygen gas can then pass through the external walls of the hollow fibers and oxygenate the blood passing within the fiber while carbon dioxide is passed out of the blood through the hollow fiber.

Alternatively, the oxygen gas may be passed into the center of the hollow fibers and the blood circulated through the casing thereby contacting the external surface of the hollow fibers.

Rather than utilizing a dual-ended tubular casing in which both ends are open to allow the passage of blood, it is possible to utilize a permeator in which hollow fiber bundles have been formed into a loop so that the ends of each of the fibers both exit through the same opening in the tubular casing.

For a further illustration of devices which can employ hollow fibers for blood oxygenation, see U.S. Patent Nos. 2,972,349; 3,373,876; and 4,031,012, the disclosures of which are herein incorporated by reference.

The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples. All parts and percentages in the claims and the remainder of the specification are by weight unless otherwise specified.

Example 1

Isotactic polypropylene having a melt index of 5, a weight average molecular weight of 380,000 and a density of 0.90 gm/cc, is melt spun through a five-hole concentric hollow jet spinneret. Each jet hole of the spinneret is of the standard tube-in-orifice type with the tube supplied with a source of low pressure air, the pressure being controlled with an air flow metering device set at 3.8 which indicates a flow rate of 120 cc/min. The outer diameter of each extrusion orifice (jet hole) of the spinneret is 1.391 mm, and the inner diameter of extrusion orifice is 0.772 mm. The diameter of the air tube within each extrusion orifice is 0.332 mm. Pellets of the polypropylene are placed in a Brabender 3/4 inch extruder and fed into the feed zone of the extruder by gravity. The extruder is provided with a metering pump to control the melt pressure of the spinneret assembly to provide a throughput through the spinneret of 23 gms/minute. The temperatures of the feed zone, metering and melt zones of the extruder are controlled by separate jacket sections. The temperature of the spinneret assembly is controlled by a separate electrically heated jacket and a constant extrusion, i.e., spin temperature of 245°C is maintained as indicated by a thermocouple in the spinneret assembly. An adjustable feed take-up device collects the extruded fibers at a take-up speed (TUS) of 500 meters/minute. The hollow precursor fibers are accordingly drawn at a drawdown or spin ratio of 100:1. The take-up roll is located 10 feet from the spinneret and the extruded fibers are quenched by passage through air at room temperature i.e., 25°C. The degree of orientation as determined by X-ray diffraction analysis as described herein is 16°. The precursor fibers exhibit an elastic recovery from 50% extension at zero recovery time, 25°C, and 65% relative humidity, of 70%, an average inner diameter of 223 microns, an average outer diameter of 257 microns and an average wall thickness of 17 microns. The resulting fibers are then annealed at constant length while still wrapped around the take-up roll by placing the take-up roll in an oven and heating them to 140°C for 30 minutes.

Samples of the annealed precursor fiber are then subjected to varying degrees of cold stretch at ambient temperatures as shown in Table I runs 1 to 6 and then to varying degrees of hot stretch at 140°C also as shown in Table I runs 1 to 6. The strain rate for both hot stretch and cold stretch is also shown at Table I. Cold and hot stretching is achieved using a conventional Bruckner stretch frame and the elevated temperatures during hot stretching are achieved by placing the stretch frame in a forced hot air oven. The hot stretched fibers are left in the oven for 30 minutes to achieve heat setting at the same temperature employed for hot stretching i.e., 140°C. The fibers are maintained at constant length during heat setting by the stretch frame.

For runs 7 to 10 the precursor fiber sample preparation is varied with respect to spin temperature, take-up speed, draw ratio, throughput rate, and air flow meter setting as shown at Table I. The degree of orientation (as determined by X-ray diffraction analysis as described herein) of the precursor fibers as prepared in accordance with runs 7 and 8 is 16° and for runs 9 and 10 is 22°. The elastic recovery (ER) from 50% extension at zero recovery time for runs 9 and 10 is 64%. The ER for runs 7 and 8 was not determined. The degree of cold stretch and hot stretch as well as the strain rate is also shown at Table I.

The resulting heat set microporous hollow fibers are then tested for surface area by nitrogen absorption as described herein and also for oxygen flux. The oxygen flux is determined in the following manner.

Twenty of the hollow microporous fibers from each run 16 inches in length are prearranged in a parallel fiber bundle configuration and then looped so that the 40 open ends of the fibers are contiguous and lie flush in a single plane. The open ends of the fiber loop are then inserted through a short length (1.25 inches) hard plastic tubing having a 1/8 inch inner diameter. The fibers are then coated with epoxy resin 5 to 6 inches from the open looped fiber ends. The plastic tubing is then slipped down over the resin coated section so that about two inches of the uncoated fiber bundle protrude out of the tubing leaving the open ends of the looped fiber bundle extending out of the tubing. When the resin has hardened the open ends of the looped fiber bundle are trimmed flush with the plastic tubing. However, to preserve the open circularity of the open fiber ends trimming is achieved by first immersing the fibers in liquid nitrogen, then dipping them in isopropyl alcohol to fill the lumens with liquid, re-immersing the fibers in liquid nitrogen for about 1.5 minutes to freeze the alcohol, and then laying them across a small wood block also immersed in the liquid nitrogen. The open ends of the fibers can then be easily trimmed with a razor against the wooden block without damage. The tubing-fiber assembly is then sealed in a 1/4 or 3/5 inch diameter Sweglok™ adapter with epoxy resin leaving a 3/4 inch extension of the tubing exposed above the adaptors. The epoxy potted fiber assembly is then inserted into a 7-inch length of 3/8 inch diameter copper tubing and the Sweglok™ adaptor sealed with appropriate fittings. For access convenience, a 3-way T-fitting is attached to the distal end of the copper tubing (with respect to the Sweglok fitting) and one of the exits of the T-fitting is sealed. One end of a rubber hose is attached to the open orifice of the T-fitting and the other end is inserted into a inverted graduated cylinder filled with water and immersed in a water bath. Oxygen gas is then passed through the open fiber ends through the fiber walls and collected in the graduate cylinder. The gas pressure is maintained first at 5 psi and then at 10 psi as shown in Table I. The gas flux (J_g) in cc/cm² . min is determined from the equation described herein.

As may be seen from the results of Table I, oxygen permeabilities or fluxes higher than about 80 cc/cm² . min can be obtained from hollow microporous fibers prepared in accordance with the process of the present invention. Such permeabilities when normalized to flux per micron of fiber wall thickness represent a substantial improvement over the normalized gas permeabilities of microporous films in flux per micron of film thickness, when such films are prepared in accordance with the cold stretch/hot stretch process of U.S. Patent No. 3,801,404.

For example, the normalized flux of the hollow microporous fibers having an oxygen gas permeability at 10 psi of 82.9 cc/cm² . min is obtained by dividing this permeability by the average fiber wall thickness of 15 microns to give a normalized flux per micron of fiber wall thickness of 5.5.

Similarly, a microporous film prepared by the cold stretch/hot stretch process of U.S. Patent No. 3,801,404 and having a film thickness of about 25.5 microns exhibits an oxygen gas flux of about 44 cc/cm² . min. When this gas flux is normalized for comparison with the normalized gas flux of the hollow microporous fibers of the subject invention a flux per micron of film thickness of 1.73 is obtained. Similar comparisons can be made with runs 1 to 9 of Example I.

Thus, hollow microporous fibers can be prepared in accordance with the process of the present invention which exhibit a normalized flux about 3 times the normalized flux of microporous films prepared by the process of the above described patent.

Table I

Run No.	Spin Temp. °C	TUS (ml/min)	Through-put (gm/min)	Draw down Ratio	Air Flow Meter Setting	Av. I.D. (μ)	Av. O.D. (μ)	Av. Wall Thickness	Cold Stretch % (25°C)	Hot Stretch % (140°C)	Strain Rate (%/min)	Av. I.D. of Fiber After Heat Setting (μ)	Av. Wall Thickness of Fiber After Heat Setting (μ)	Surface Area (m ² /gm)	Oxygen Flux (cc/cm ² ·min)
															5 psi 10 psi
1	245	500	23	100	3.8	223	257	17	20	80	20	161	16	26.9	18.5 44.6
2	245	500	23	100	3.8	223	257	17	20	80	20	161	16	24.4	19.2 45.1
3	245	500	23	100	3.8	223	257	17	20	60	16	166	16	18.8	18.6 51.0
4	245	500	23	100	3.8	223	257	17	20	60	16	166	16	19.8	24.2 53.5
5	245	500	23	100	3.8	223	257	17	20	100	25	152	17	18.1	24.8 55.8
6	245	500	23	100	3.8	223	257	17	20	100	25	152	17	18.1	22.1 46.9
7	245	335	22	72	3.8	264	300	18	20	80	20	215	14	37.7	29.7 60.0
8	245	335	22	72	3.8	264	300	18	20	80	20	215	14	37.7	31.8 74.8
9	250	200	20	48	3.0	278	314	21	20	80	20	205	15	32.3	31.5 67.8
10	250	200	20	48	3.0	278	314	21	20	80	20	205	15	26.4	40.1 82.9

Comparative Example I

Example I is repeated with the exception that the inner diameter of the precursor fiber is reduced to below 140 microns as shown at Table II. The degree and strain rate of the cold stretching and hot stretching as well as the processing variables are also summarized at Table II. Note that the

5 microporous hollow fiber wall thickness is assumed to remain substantially unchanged and has not been measured empirically. 5

Runs 1 to 10 illustrate the reduced oxygen permeability obtained when the precursor fiber inner diameter averages substantially below 140 microns, e.g., about 86 microns, as compared to the gas permeability obtained from the runs of Example I employing precursor fiber inner diameters in excess of 10 140 microns. The highest oxygen flux obtained was only 10.1 cc/cm² . min. 10

Runs 7 to 10 illustrate a substantial reduction in gas permeability when the hot stretch step is eliminated or the extension ratio is selected so that the degree of cold stretch is greater than the degree of hot stretch.

Runs 11 to 14 illustrate unsuccessful attempts to improve the gas permeability of cold stretched 15 fibers by allowing them to relax 10% (i.e., Runs 11 & 12) and by allowing the cold stretched fibers to relax 10% at a temperature of 130°C (i.e., runs 13 & 14). 15

Runs 15 to 26 illustrate the gas permeabilities achieved at varying process conditions by employing average inner precursor fiber diameters of 110 microns. As may be seen therefrom the gas permeability is substantially reduced in comparison to the gas flux of precursor fibers having average 20 inner diameters employed in the runs of Example 1. 20

Table II

Run No.	Spin Temp. °C	TUS (m/min)	Throughput (gm/min)	Drawdown Ratio	Air Flow Meter Setting	Av. I.D. (μ)	Av. O.D. (μ)	Av. Wall Thickness (μ)	Cold Stretch % (25°C)	Hot Stretch % (140°C)	Strain Rate %/min	Set-ting*** (μ)	Surface Area (m ² /gm)	Oxygen Flux (cc/cm ² ·min) 5 psi 10 psi
1	250	500	17	140	4.0	86.2	125.5	19.6	20	80	100	64.6	35.1	5.1 9.5
2	250	500	17	140	4.0	86.2	125.5	19.6	20	80	100	64.6	32.3	4.0 10.1
3	250	500	17	140	4.0	86.2	125.5	19.6	20	80	20	64.6	41.1	4.0 9.4
4	250	500	17	140	4.0	86.2	125.5	19.6	20	80	20	64.6	37.7	3.2 9.0
5	250	500	17	140	4.0	86.2	125.5	19.6	20	80	10	64.6	29.1	5.1 11.9
6	250	500	17	140	4.0	86.2	125.5	19.6	20	80	10	64.6	40.2	3.6 8.3
7	250	500	17	140	4.0	86.2	125.5	19.6	100	0	20	64.6	27.9	1.1 2.4
8	250	500	17	140	4.0	86.2	125.5	19.6	100	0	20	64.6	21.7	1.4 2.9
9	250	500	17	140	4.0	86.2	125.5	19.6	95	10	20	64.6	23.7	1.4 3.4
10	250	500	17	140	4.0	86.2	125.5	19.6	95	10	20	64.6	23.7	1.9 4.1
11	245	500	14	168	4.3	110*	137.5	13.5	110	0	22	82.5	26.2	1.8 4.1
12	245	500	14	168	4.3	110*	137.5	13.7	110	0	22	82.5	19.6	0.6 1.3
13	245	500	14	168	4.3	110**	137.5	13.7	110	0	22	82.5	9.4	7.3 15.7
14	245	500	14	168	4.3	110**	137.5	13.7	110	0	22	82.5	13.2	3.4 7.4
15	245	500	14	168	4.3	110	137.5	13.7	20	50	14	82.5	31.5	10.1 23.5
16	245	500	14	168	4.3	110	137.5	13.7	20	50	70	82.5	28.5	11.4 23.5
17	245	500	14	168	4.3	110	137.5	13.7	20	50	140	82.5	30.8	10.2 23.3
18	245	500	14	168	4.3	110	137.5	13.7	20	65	17	82.5	ND	10.5 29.6
19	245	500	14	168	4.3	110	137.5	13.7	20	80	20	82.5	32.8	13.7 28.0
20	245	500	14	168	4.3	110	137.5	13.7	20	100	24	82.5	ND	7.3 17.0
21	245	500	14	168	4.3	110	137.5	13.7	20	110	26	82.5	40.3	9.6 20.5
22	245	500	14	168	4.3	110	137.5	13.7	20	110	130	82.5	37.8	8.7 18.2
23	245	500	14	168	4.3	110	137.5	13.7	20	125	29	82.5	35.5	10.0 21.0
24	245	500	14	168	4.3	110	137.5	13.7	20	125	145	82.5	33.9	9.7 22.1
25	245	500	14	168	4.3	110	137.5	13.7	20	135	155	82.5	35.5	10.1 23.4
26	245	500	14	168	4.3	110	137.5	13.7	20	135	31	82.5	27.6	10.8 24.4

* Fibers are allowed to relax 10% after cold stretching.

***Fiber inner diameter determined from calculations based on assumption that precursor fiber ID shrinks about 25% during processing

** Fibers are allowed to relax 10% at 130°C.

ND=Not determined

Comparative Example II

Example I Run 1 is repeated with respect to the preparation of the precursor fiber. Precursor fiber samples are then annealed at 140°C, for 30 minutes at constant length, cold stretched 100% at a strain rate of 20%/min and a temperature of 25°C and then heat set at different temperatures of 140°C, 145°C, 150°C, and 155°C for 30 minutes. When the heat set temperature is the same as the annealing temperature, i.e., 140°C, the fibers shrink and curl up. At a heat set temperature slightly above the annealing temperature, i.e., 145°C the fibers shrink but to a lesser extent. When the heat set temperature is 150 or 155°C no shrinkage is observed. If the heat set time employed at 150°C and 155°C is lowered substantially below 30 minutes, shrinkage will again be observed.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

15 Claims

1. A process for preparing hollow open-celled polypropylene microporous fibers having an oxygen flux of at least 35 cc/cm² . min at 10 psi comprising:
 - (A) melt spinning at a temperature of at least 230°C isotactic polypropylene having a melt index of at least 1 in a manner sufficient to obtain hollow nonporous polypropylene precursor fibers, taking up said precursor fibers at a drawdown ratio of at least about 40, said melt spinning being conducted in a manner sufficient to impart to said precursor fibers after take-up an average inner diameter of at least about 140 microns, an average inner diameter to average wall thickness ratio of from about 8:1 to about 40:1, a degree of orientation as determined from the half width of a wide angle (110) X-ray diffraction arc of not greater than 25°, and an elastic recovery from 50% extension at 25°C, 65% relative humidity, and at zero recovery time, of at least 50%;
 - (B) annealing the precursor fibers at a temperature between about 50°C and less than 165°C for a period of about 0.5 second to about 24 hours;
 - (C) cold stretching the nonporous precursor hollow fibers in the direction of their length at a temperature greater than the glass transition temperature of the precursor fiber and not greater than about 100°C to impart porous surface regions to the walls of the fiber which are perpendicular to the cold stretching direction;
 - (D) hot stretching the annealed cold stretched hollow fibers of (C) in the same direction of cold stretch at a temperature above the cold stretching temperature and below the melting point of the polypropylene to impart an open-celled microporous configuration to the hollow fiber walls, said degree of cold stretching and hot stretching being conducted in a manner sufficient to control the average inner diameter of the resulting hot stretched hollow microporous fibers to at least 100 microns and to achieve a total degree of combined stretching of from about 80 to about 200%, an extension ratio of from about 1:3 to about 1:20, and a strain rate of from about 10 to about 200%/minute;
 - (E) heat setting the resulting hot stretched fibers of (D) under tension to produce dimensionally stable open-celled hollow microporous fibers having an average inner diameter of at least 100 microns.
2. The process of Claim 1 wherein the melt spinning temperature is from about 240 to about 280°C, the drawdown ratio at which the hollow precursor fibers are taken up is at least about 40, the average inner diameter of the hollow precursor fibers after take-up is controlled to be from about 140 to about 400 microns, the cold stretching is conducted at a temperature of from about 15 to about 70°C, the hot stretching is conducted at a temperature of about 130 to about 145°C, the total degree of combined cold and hot stretching is from about 80 to about 155%, and the extension ratio is from about 1:3 to about 1:10.
3. The process of Claim 1 wherein the melt spinning temperature is from about 240 to about 250°C.
4. The process of Claim 1 wherein hot stretching and heat setting are combined into a single step by sequentially hot stretching the cold stretched hollow fibers in a plurality of discrete stretching steps.
5. A process for preparing hollow polypropylene open-celled microporous fibers having an oxygen flux of at least 35 cc/cm² . min at 10 psi comprising:
 - (A) melt spinning at a temperature of about 240 to about 280°C isotactic polypropylene having a melt index of at least about 5 in a manner sufficient to obtain hollow nonporous polypropylene precursor fibers, taking up said hollow precursor fibers at a drawdown ratio of from about 40 to about 100, said melt spinning also being conducted in a manner sufficient to impart to said precursor fibers after take-up an average inner diameter of from about 200 to about 300 microns, an average inner diameter to average wall thickness ratio of from about 10:1 to about 30:1, a degree of orientation as determined from the half width of a wide angle (110) X-ray diffraction arc of not greater than 25°, and an elastic recovery from 50% extension at 25°C, 65% relative humidity, and at zero recovery time, of at least 50%;

(B) annealing the hollow precursor fibers at a temperature of about 130 to about 145°C for about 30 minutes;

(C) cold stretching the nonporous precursor hollow fibers in the direction of their length at a temperature of from about 15 to about 70°C, a degree of stretch of about 20% based on the original precursor fiber length, and a strain rate of from about 10 to about 100%/minute to impart porous surface regions to the walls of the fiber which are perpendicular to the cold stretching direction;

(D) hot stretching the cold stretched hollow fibers of (C) in the same direction of cold stretch at a temperature of about 130 to about 145°C, a degree of stretch of about 60 to about 100%, and a strain rate of about 10 to about 100%/minute to impart an open-celled microporous configuration to the hollow fiber walls;

(E) heat setting the resulting hollow fibers under tension at a temperature of about 130 to about 160°C to produce dimensionally stable open-celled hollow microporous fiber having an average inner diameter of at least 100 microns.

6. Hollow polypropylene open-celled microporous fibers having an oxygen flux of at least 35 cc/cm² . min at 10 psi prepared by a process which comprises:

(A) melt spinning at a temperature of at least 230°C isotactic polypropylene having a melt index of at least 1 in a manner sufficient to obtain hollow nonporous polypropylene precursor fibers, taking up said precursor fibers at a drawdown ratio of at least about 40, said melt spinning being conducted in a manner sufficient to impart to said precursor fibers after take-up an average inner diameter of at least about 140 microns, an average inner diameter to average wall thickness ratio of from about 8:1 to about 40:1, a degree of orientation as determined from the half width of a (110) X-ray diffraction arc of not greater than 25°, and an elastic recovery from 50% extension at 25°C, 65% relative humidity, and zero recovery time, of at least 50%;

(B) annealing the precursor fibers at a temperature between about 50°C and less than 165°C for a period of about .5 second to about 24 hours;

(C) cold stretching the nonporous precursor hollow fibers in the direction of their length at a temperature greater than the glass transition temperature of the precursor fiber and not greater than about 100°C to impart porous surface regions to the walls of the fiber which are perpendicular to the cold stretching direction;

(D) hot stretching the annealed cold stretched hollow fibers of (C) in the same direction of cold stretch at a temperature above the cold stretching temperature and below the melting point of the polypropylene to impart an open-celled microporous configuration to the hollow fiber walls, said degree of cold stretching and hot stretching being conducted in a manner sufficient to control the average inner diameter of the resulting hot stretched hollow microporous fibers to at least 100 microns and to achieve a total degree of combined stretching of from about 80 to about 200%, an extension ratio of from about 1:3 to about 1:20, and a strain rate of from about 10 to about 200%/minute;

(E) heat setting the resulting hot stretched fibers of (D) under tension to produce dimensionally stable open celled hollow microporous fibers having an average inner diameter of at least 100 microns.

7. A process which comprises employing the hollow polypropylene open celled microporous fibers of Claim 6 in a blood oxygenator device.

8. A process according to Claim 1 when carried out substantially as described in Example 1.

9. Hollow polypropylene open-celled microporous fibres having an oxygen flux of at least 35 cc/cm² . min at 10 psi when prepared by the process of any of Claims 2 to 5 and 8.

10. A process which comprises employing the hollow polypropylene open celled microporous fibres of Claim 6 in a blood oxygenator device.